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THIN FILM HEATING ELEMENT

BACKGROUND OF THE INVENTION

This invention relates to heating elements of the kind including an electrically conductive metal oxide film on an electrically insulating substrate.

Such devices are known, and may for example consist of a thin film of tin oxide deposited on a glass substrate by means of pyrolitic deposition.

If such thin film heating elements are to be used in electrical appliances such as cooktops, it is desirable that they be capable of operating at high temperatures, up to 650°C. In applications such as electric kettles where the heating element is small, the element must be capable of handling high power densities, of the order of 10- 20 Watts cm^{-2}. Prior art devices have not proved satisfactory in these conditions. It has been found by the present applicants that tin oxide layers tend to become unstable with increasing temperature, due to the tendency for the oxide to change state. It has also been found that where fluorine is employed as an electron donor or conductivity carrier the properties of the film change irreversibly with increasing temperature, apparently due to the fluorine tending to leave the film at temperatures above 400°C.

We have also found that the tin chloride solutions used in the prior art, for example in the spray pyrolysis process, are not stable in conditions of high humidity due to their hygroscopic properties, and this can lead to lack of uniformity in the oxide films produced.

US Patent No. 4,889,974 of Auding, *et al.* describes thin film elements intended for temperatures beyond 600°C, using oxide films doped at high levels with pairs of compensating foreign atoms. The metal oxide films are doped with, maximally, 10 mol % of each of the foreign atoms compensating each other in pairs, the quantity of said acceptor-forming elements and said donor-forming elements differing maximally

by 10%. The Auding patent describes the use of indium, boron, aluminium or zinc as the acceptor-forming dopant, and antimony or fluorine as the donor-forming dopant.

However, these films using stannic chloride have been found to be difficult to deposit in humid atmospheres and have been found to be unstable in the power densities of approximately 20 Watts per cm^2 required for rapid rise-time applications.

To the applicants' knowledge the films described in the Auding patent have not seen commercial use and are known only from this document.

SUMMARY OF THE INVENTION

The present applicants have found that a metal oxide layer of satisfactory stability in high power density applications may be obtained by doping with at least one and preferably two rare earth elements. The rare earth dopants are preferably cerium and lanthanum. Preferably these two rare earths are present in substantially equal concentrations. The presence of the rare earth dopants in the thin film layer has been found by the present applicants to have the effect of stabilising the oxidation state of the metal.

We have also found that stability at high temperatures may be obtained by further doping with equal quantities of donor and acceptor elements, and by avoiding the use of fluorine as a dopant. The preferred donor and acceptor elements for this purpose are respectively antimony and zinc.

In one aspect, the invention resides in a thin film electrical heating element including a layer of an electrically conducting metal oxide on an electrically insulating substrate, said metal oxide layer being doped with at least one rare earth element.

Preferably the metal oxide is deposited on the substrate by pyrolysis of an organometallic base solution containing the at least one rare earth element.

In a preferred form the metal oxide layer is tin oxide and contains two rare earth elements such as cerium and lanthanum.

This aspect of the invention provides a thin film heating element which is capable of withstanding power densities of up to 10-20 Watts cm^{-2} and/or temperatures in excess of 600°C.

In another aspect, the invention resides in a method for the manufacture of a thin film heating element including the step of depositing a layer of metal oxide onto an electrically insulating substrate by pyrolysis of an organometallic base solution containing at least one rare earth element.

Preferably the base solution contains both cerium and lanthanum in concentrations up to 5 mol %.

We have found that superior results can be obtained if the film is prepared by spray pyrolysis from a solution of monobutyl tin trichloride. The stability of this material in high humidity enables consistent results to be obtained across varying atmospheric conditions, by reducing premature oxidation.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is graph showing the power dissipation versus time relationship for a thin film heating element made according to the invention.

Fig. 2 shows the relationship between temperature and power at steady state for five elements having power ratings between 500 and 1330 watts.

DESCRIPTION OF PREFERRED EMBODIMENTS

While some benefit will be obtained from quite low concentrations of the rare earth dopant, minimal effects will be observed with concentrations in the pyrolysis solution

of 0.01 mol %, preferred concentrations of each of the cerium and lanthanum are between approximately 1.25 mol % and approximately 3.75 mol %. Preliminary tests have shown that stability of the metal oxide layer is maximised when substantially equal concentrations of two rare earth elements, such as cerium and lanthanum, are used. Generally speaking the concentration of these rare earths will be chosen as that which contributes to film stability at the power densities for which the film is intended. Best results for films intended for operation at 20 Watts cm^{-2} have been obtained using equal concentrations of approximately 2.5 mol %.

The film is preferably doped with substantially equal quantities of donor and acceptor elements, the preferred dopants being antimony and zinc. The concentrations of both antimony and zinc will be influenced by the resistivity which is required. We have found base solution concentrations for these materials in the region of 2.8 mol % to be suitable for heating element applications.

A useful characteristic of such films in their application as heating elements arises from the positive temperature coefficient resistance of the film. This enables elements to be produced which are self-regulating, in that they will initially operate at a higher wattage and, with increasing temperature, stabilise at the lower design wattage.

The substrate material will of course be chosen to suit the application. Suitable substrates include glass ceramics, silicon nitrides and other ceramic substrates as well as metallic substrates coated with high-temperature stable, electrically-insulating materials.

The preferred substrate temperatures for applying the base solution with dopants range from 500 to 750°C. Preferably, for application at 500°C, post annealing at approximately 600°C for at least one hour is carried out to assist in stabilising the film.

Films according to this invention were manufactured from a solution using the spray pyrolysis process. For this purpose, monobutyl tin trichloride was used as a base

solution, with 2.8 mol % antimony chloride, 2.8 mol % zinc chloride, 2.5 mol % cerium and 2.5 mol % lanthanum.

These films were fabricated with effective resistances of 26 ohm, 30 ohm and 45 ohm to enable heaters of 2.2 kW, 1.8 kW and 1.2 kW respectively to be used, powered by a 240V mains supply voltage. The films were selectively deposited using high temperature masking inks which were removed by brushing after deposition of the film. The films deposited had a high degree of transparency. The resistive properties of the heating elements remained unchanged after 3500 cycles (40 minutes on and 20 minutes off) at 650°C.

As indicated above, the positive temperature coefficient of resistance of these elements enables a self-regulating characteristic to be obtained, with an initially high power dissipation which may be of advantage in achieving more rapid rise to operating temperature. Fig. 1 shows the typical behaviour of the elements, where power dissipation is plotted against time of operation. As will be observed, the dissipation of the element commences at a high level and decreases as the resistance of the element increases with temperature, until a steady state condition is achieved at the design power consumption. Upon temporary cooling of the element, for example through contact with a cooler body to be heated, power dissipation will temporarily increase, assisting in achieving rapid heating.

Fig. 2 shows the relationship between temperature and power at steady state for five elements having power ratings between 500 and 1330 watts.

Life tests have shown that the films are particularly stable on inert substrates like quartz 96% silica in temperatures up to 650°C with power densities in excess of $15.5W/cm^2$. The films on lower grades of glass ceramics having alkali impurities such as lithium and sodium were stable to 500°C at extremely high power densities.

Sheet resistances varying from around 60 ohms to above 400 ohms have been fabricated by varying the number of spray passes. The thin film thickness could be

varied between 2000 Angstrom Units to around 14000 Angstrom Units by varying the number of spray passes. The films were deposited on various substrates including glass ceramics, alumina, silica glass and silicon nitride.

As well as their suitability in high temperature and/or high rise time applications, films made in accordance with the invention may be used in low temperature applications, such as comfort heating, refrigerating defrost, and general heating. Heating elements of tubular shape manufactured using the above technology can be used in heat exchangers for flow applications, air-conditioning re-heaters, hair dryers, washing and drying appliances, and can also be used as radiating surfaces.

While particular embodiments of this invention have been described, it will be evident to those skilled in the art that the present invention may be embodied in other specific forms without departing from the essential characteristics thereof. The present embodiments and examples are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.